Biaryl Formation in the Photochemical Reaction of Halogenated Aromatic Nitriles with Methoxybenzenes

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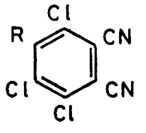
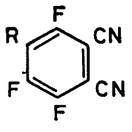
Summary Irradiation of tetrachloro- and tetrafluorophthalonitriles in the presence of anisole, 1,3-dimethoxybenzene, or 1,4-dimethoxybenzene, led to formation of biaryls, a similar process occurred with mixtures of 1,4-dimethoxybenzene and 2- or 4-chlorobenzonitrile, but not 3-chlorobenzonitrile.

IRRADIATION of tetrachlorophthalonitrile (TCPN, **1**, R=Cl) and tetrafluorophthalonitrile (TFPN, **2**, R = F) in the presence of aliphatic ethers leads to replacement of the 4-halogeno substituent by an α-alkoxyalkyl group derived from the ether[1] We now report that reaction with aromatic ethers leads to formation of biaryls, a process that does not appear to have been previously reported from direct excited state interaction between an aryl halide and an aryl ether.

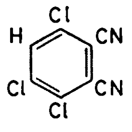


(1)



(2)

(a) R = 2-MeOC$_6$H$_4$
(b) R = 4-MeOC$_6$H$_4$
(c) R = 2,4-(MeO)$_2$C$_6$H$_3$
(d) R = 2,6-(MeO)$_2$C$_6$H$_3$
(e) R = 2,5-(MeO)$_2$C$_6$H$_3$



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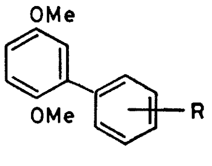
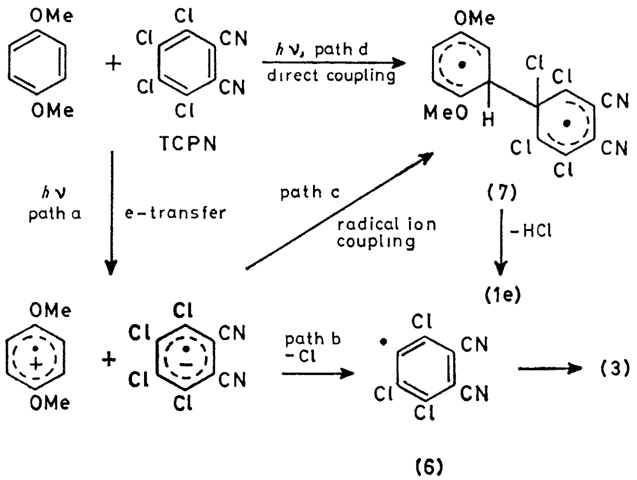


(4) R = 2-CN
(5) R = 4-CN

The Table shows the products obtained by irradiation of TCPN and TFPN in the presence of anisole, 1,3-dimethoxybenzene, and 1,4-dimethoxybenzene; the products obtained by irradiation of mixtures containing 1,4-dimethoxybenzene and 2-chlorobenzonitrile or 4-chlorobenzonitrile are also included. 3-Chlorobenzonitrile was unreactive under similar conditions.

The relative importance of dehalogenation *vs.* biaryl formation for the chloroaromatic nitriles seems to depend on the relative donor–acceptor abilities of the reactants. Thus, the powerful acceptor TCPN forms only biaryls with anisole (oxidation potential 40·6 kcal mol^{-1})[2] whereas with the better donors 1,3- and 1,4-dimethoxybenzenes (34·4 and 30·9 kcal mol^{-1}, respectively)[2] both dehalogenation and biaryl formation occurs. However, 2- and 4-chlorobenzonitriles, considerably weaker acceptors than TCPN, exhibit only biaryl formation with 1,4-dimethoxybenzene.



SCHEME

These reactions may be explained within the framework of the Scheme, which illustrates the reaction of TCNP with 1,4-dimethoxybenzene. Electron transfer (path a), followed by loss of chloride from the TCPN radical anion (path b), would account for the formation of the dehalogenation product (**3**) *via* the intermediacy of the aryl radical (**6**). Radical ion coupling (path c) would lead to the biaryl (**1e**) *via* the biradical (**7**). Alternatively, or additionally, the biaryl (**1e**) could be formed *via* a direct coupling route (path d) which does not involve a discrete radical cation/radical anion pair.

The inclusion of an electron transfer process (path a) seems necessary to explain the formation of the dehalogenation product (**3**) in the TCPN–1,3-dimethoxybenzene and TCPN–1,4-dimethoxybenzene reactions. However, no such simple dehalogenation process competes with biaryl formation in (i) the TCPN–anisole reaction, (ii) the 2-chlorobenzonitrile–1,4-dimethoxybenzene reaction, or (iii) the 4-chlorobenzonitrile–1,4-dimethoxybenzene reaction. In these cases, electron transfer leading to formation of a radical anion does not appear to be operative. Rather, a

TABLE. Photoproducts[a] from halogenated aromatic nitriles and methoxybenzenes.

Reactants[b,c]		Products[d]	
Halogenonitrile	Methoxybenzene	Biaryls	Dehalogenation
TCPN	Anisole	(**1a**) (60%) + (**1b**) (18%)	—
TCPN	1,3-Dimethoxybenzene	(**1c**) (25%) + (**1d**) (3%)	(**3**) (13%)
TCPN	1,4-Dimethoxybenzene	(**1e**) (6%)	(**3**) (65%)
TFPN	Anisole	(**2a**) (40%) + (**2b**) (10%)	—
TFPN	1,3-Dimethoxybenzene	(**2c**) (30%) + (**2d**) (25%)	—
TFPN	1,4-Dimethoxybenzene	(**2e**) (36%)	—
2-ClC$_6$H$_4$CN	1,4-Dimethoxybenzene	(**4**) (21%)	—
4-ClC$_6$H$_4$CN	1,4-Dimethoxybenzene	(**5**) (78%)	—
3-ClC$_6$H$_4$CN	1,4-Dimethoxybenzene	No reaction occurred	

[a] All products gave satisfactory microanalytical and spectroscopic data. ^{19}F and ^{1}H n.m.r. spectroscopy allowed the relative orientations of substituents to be determined. The assumption of 4-substitution in TCPN was supported by the conversion of (**2a**) into (**1a**) on heating with lithium chloride in *N*-methylpyrrolidone. [b] Irradiations with TCPN and TFPN were in dichloromethane solution, $\lambda > 300$ nm. [c] Irradiations with the chlorobenzonitriles were in hexane solution, $\lambda > 230$ nm. [d] Yields are based on the amount of halogenonitrile consumed during photolysis and are quoted for recrystallised products obtained following chromatography.

direct coupling pathway, analogous to path d in the Scheme, seems preferable. Such a process would produce biradicals [analogous to (**7**)] from TCPN, TFPN, 2-chlorobenzonitrile, and 4-chlorobenzonitrile which experience stabilisation owing to the presence of a 2- or 4-cyano group. The lack of a suitably sited cyano substituent may account for the non-participation of 3-chlorobenzonitrile in product formation.

These reactions are related to those of 1,2,4,5-tetracyanobenzene (TCNB) with aromatic hydrocarbons,[3] of hexafluorobenzene with benzene,[4] and of aromatic ethers with acrylonitriles.[5] It is interesting to note that, whilst TCNB is similar to TCPN and TFPN in its reactions with aliphatic ethers,[1,6] TCNB has been reported[2] not to react photochemically with anisole.

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